+69.2° (H_2O, *c* 0.39), R_f 0.39 (Si gel; $CHCl_3$–MeOH–Me_2CO–H_2O, 3:3:3:1).

2',3',4',6'-Tetraacetyl cinncassiol D_4 glucoside (**6**). Compound **2** (15 mg) was acetylated with Ac_2O (2 ml) and pyridine (3 ml) for 30 min at room temp. to give the acetate (**6**) (11 mg). An amorphous powder; $[\alpha]_D^{21}$ −5.7° (MeOH; *c* 1.05), EIMS *m/z*: 682 $[M]^+$, 664, 646, 603, 587, 331, 316, 298, 257, 255, 239, 176, 169, 157, 115, 109, ^1H NMR (C_5D_5N): δ 1.04, 1.21 (each 3H, *d*, *J* = 7 Hz, 18-Me_2), 1.28 (3H, *d*, *J* = 7 Hz, 1-Me), 1.31 (3H, *s*, 9-Me), 1.72 (3H, *s*, 12-Me), 1.98, 2.00, 2.05 (12H, all *s*, 4× –OAc), 4.38 (1H, *br s*, 6-H); ($CDCl_3$): δ 0.94 (6H, *d*, *J* = 7 Hz, 18-Me_2), 0.98 (3H, *s*, 9-Me), 1.02 (3H, *d*, *J* = 6 Hz, 1-Me), 2.00, 2.04, 2.06 (12H, all *s*, 4× –OAc), 3.75 (1H, *br s*, 6-H), 4.51 (1H, *d*, *J* = 7 Hz, 1'-H).

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DITERPENES FROM *BALLOTA* SPECIES

GIUSEPPE SAVONA, MAURIZIO BRUNO, FRANCO PIOZZI and CLAUDIA BARBAGALLO*

Istituto di Chimica Organica, Università di Palermo, 20 via Archirafi, 90123 Palermo, Italy; *Istituto di Botanica, Università di Catania, 95125 Catania, Italy

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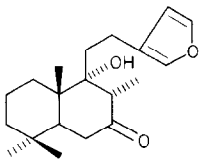
Key Word Index—*Ballota andreuzziana*; *B. pseudodictamnus*; Labiatae; diterpenes; hispanolone; ballonigrin; 18-hydroxyballonigrin; marrubenol; 5-hydroxy-7, 4'-dimethoxyflavone.

Abstract—Hispanolone was isolated from *Ballota andreuzziana*; *B. pseudodictamnus* contains ballonigrin, 18-hydroxyballonigrin, marrubenol, and the flavone 7, 4'-di-*O*-methylapigenin.

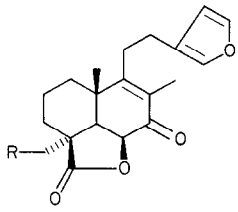
During a chemotaxonomic investigation of the genus *Ballota*, we have reported several new furanoid diterpenes in *B. nigra* [1–3], *B. rupestris* [2, 4], *B. hispanica* [5, 6], *B. lanata* [7] and *B. acetabulosa* [8]. Continuing this work, we have now extracted the species *B. andreuzziana* Pampan. and *B. pseudodictamnus* (L.) Bentham.

Usual chromatographic work-up of the acetone extract of the aerial part of *B. andreuzziana*, collected in Cyrenaica (Libya), gave only one diterpene, identified as the known hispanolone **1** occurring in *B. hispanica* [5].

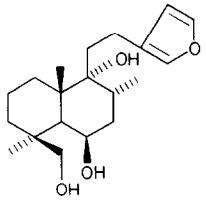
Examination of a sample of *B. pseudodictamnus*, collected in Cyrenaica (Libya), yielded three known diterpenes; ballonigrin **2**, also occurring in *B. nigra* [2], *B. rupestris* [2], *B. lanata* [7]; 18-hydroxyballonigrin **3**, isolated from *B. acetabulosa* [8]; marrubenol **4** (in traces), previously found in *Marrubium vulgare* (Labiatae) [9]. From the same source, we isolated the known 7, 4'-di-*O*-methylapigenin (5-hydroxy-7, 4'-dimethoxyflavone) [10]. Another sample of *B. pseudodictamnus*, collected in Greece near Athens, contained the same products, but marrubenol occurred in rather richer amounts.



1



2 R = H
3 R = OH



4

The occurrence of marrubenol in *B. pseudodictamnus* seems to indicate a relative closeness between the genera *Ballota* and *Marrubium*; traces of marrubiin have been found already in *B. nigra* [1]. The more noteworthy chemotaxonomic difference between the two genera remains the occurrence in all the *Ballota* diterpenes having the labdane skeleton of an oxygen function on C-7.

EXPERIMENTAL

General details for extraction have been described in previous papers [1, 11].

The sample of *B. andreuzziana* was collected in Cyrenaica (Libya) by Prof. F. Furnari (University of Catania, Institute of Botany) in May 1981; voucher specimen is deposited in the Herbarium of the Institute. The aerial part (300 g) extracted with cold Me_2CO yielded hispanolone **1** (500 mg), identified by conventional methods (mmp, IR, MS, NMR) on comparison with an authentic specimen.

The Libyan sample of *B. pseudodictamnus* was collected in Cyrenaica by Prof. F. Furnari in May 1981; voucher specimen is deposited in the Herbarium of the Institute of Botany, University of Catania. The aerial part (800 g) gave ballonigrin **2** (250 mg), 18-hydroxyballonigrin **3** (200 mg), marrubenol **4** (traces) and 7, 4'-di-*O*-methylapigenin (5-hydroxy-7, 4'-dimethoxyflavone) (50 mg). The diterpenes were identified by comparison (mmp, IR, MS, NMR) with authentic specimens; the flavone gave data (mp, MS, NMR) in agreement with those reported [12, 13] in literature.

The Greek sample of *B. pseudodictamnus* was collected near Athens in July 1979 by Dr. St. Diamantoglou, Institute of General Botany, University of Athens. The aerial part (1.400 kg) yielded comparable amounts of ballonigrin, 18-hydroxyballonigrin and 7, 4'-di-*O*-methylapigenin, and about 15 mg of marrubenol.

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